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Study on the Claisen Rearrangement. VI.[1] Catalytic Effect of Alkali Metal Salts on the Claisen Rearrangement of Allyl *o*- or *p*-Hydroxyphenyl Ether

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The Claisen rearrangement of allyl *o*- or *p*-hydroxyphenyl ether is catalyzed by alkali metal salts. The mechanism of the catalytic effect is different from that by Lewis acids such as zinc chloride. It is considered that the hydroxyl group is dissociated into phenoxide ion -O$^-$ with loss of its proton through attack by the anion residue of an alkali metal salt. Thus, the catalytic effect is attributable to a strong electron-releasing effect of phenoxide ion -O$^-$. Furthermore, for the *o*-isomer, an intramolecular repulsion between the phenoxide ion -O$^-$ and the ethereal oxygen operates.

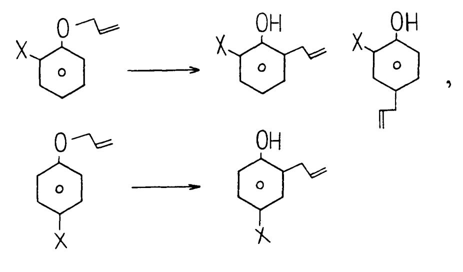
Usually, the Claisen rearrangement is a thermal reaction. However, the rearrangement is accelerated through acid catalysis.[2,3] The authors found an accelerated effect by zinc chloride for the rearrangement of allyl (substituted phenyl) ether (x-APE) and discussed the mechanism.[4] In the transition state of the Claisen rearrangement, the electron density of the ethereal oxygen of allyloxyl group increases.[5] However, in the presence of zinc chloride, the high electron density is reduced by the coordination of the salt to the ethereal oxygen. Therefore, the transition state is stabilized, and the reaction is accelerated.

In this research, alkali metal salts were used as catalysts for the Claisen rearrangement of x-APE. For an methoxy derivative (OCH$_3$-APE), no catalytic effects by these salts were noticed. However, the rearrangement of hydroxy derivatives (OH-APE) was strongly catalyzed by these salts. The mechanism of this catalytic effect is discussed.

Experimental

Preparation of Materials. The preparation and physical properties of x-APE were reported in the preceding papers.[5,6)]

Measurements on the Claisen Rearrangement. The Claisen rearrangement was carried out in a small glass ampoule as described in a previous paper.[7] x-APE and an alkali metal salt were put into an ampoule with a solvent (methanol or water-methanol). The solvent was 20 times and the catalyst (alkali metal salt) was 0.1—0.5 time in mol as much as the x-APE. The ampoule was heated at a constant temperature in an oil bath. After a measured time, the reaction mixture was cooled. The solvent was evaporated from the reaction mixture. The residue was acidified with 10% HCl and extracted with ether. The amounts of the unreacted material and products were determined by GLC. For *o*-x-APE, the conversion amount is defined as the sum of those of *o*- and *p*-rearranged products.



Results and Discussion

For the Claisen rearrangement of *o*-OH-, *o*-OCH$_3$-, and *p*-OH-APEs, the catalytic effect by sodium acetate is shown in Fig. 1, where the magnitude of catalytic effect is defined as the difference between the conversion amounts in the presence and absence of the salt. For *o*-OH-APE, the catalytic effect is observed, increasing with a increasing amount of sodium acetate. For *o*-OCH$_3$-APE, the catalytic effect is quite small. For *p*-OH-APE, the catalytic effect is observed.

The catalytic effect by sodium acetate will be compared with that by zinc chloride.[4] As shown in Fig. 2, for the methoxy derivative, the effect by sodium acetate is much smaller than that by zinc chloride. However, for the *p*-hydroxy derivative, sodium acetate accelerates the reaction by far more than zinc chloride. It may thus be considered that the mechanism of the

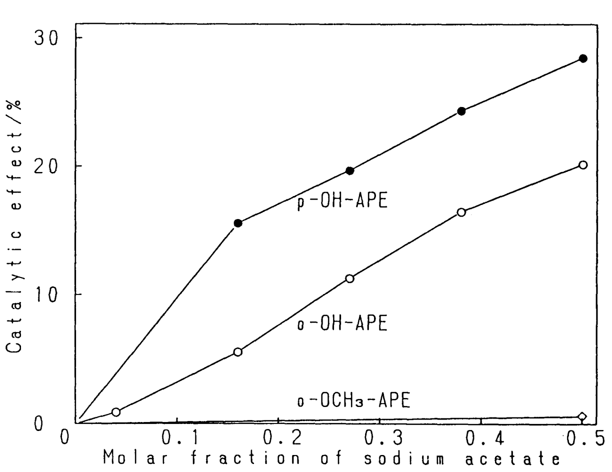


Fig. 1. The catalytic effect of CH$_3$COONa for the conversion of x-APE (solv.: CH$_3$OH, reaction time: 1 h, reaction temperature: 145 °C (*o*-isomer), 160 °C (*p*-isomer)).

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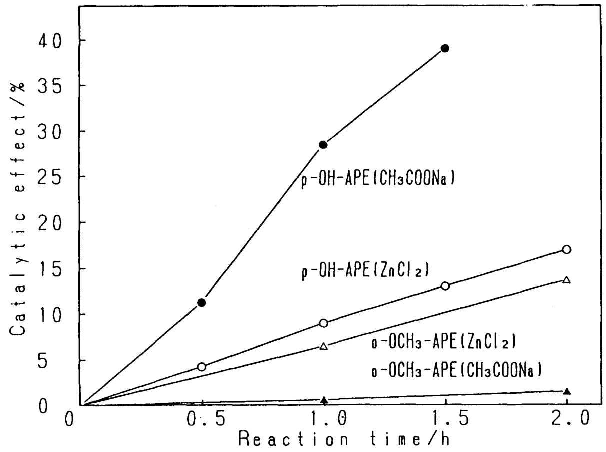


Fig. 2. The catalytic effect of CH_3COONa and $ZnCl_2$ for the conversion of x-APE (solv.: CH_3OH, salt: APE=0.5 : 1, reaction temperature: 145 °C (*o*-isomer), 160 °C (*p*-isomer)).

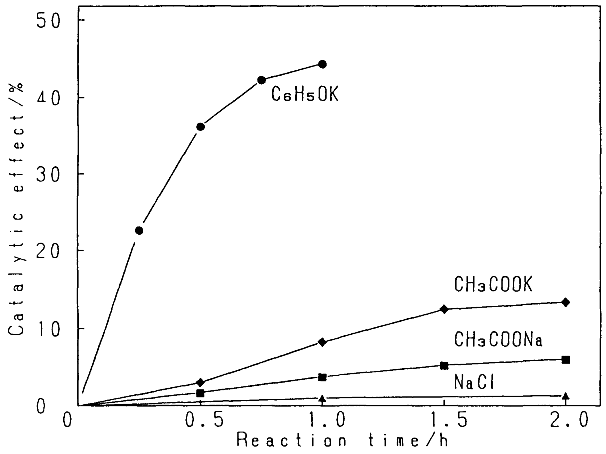


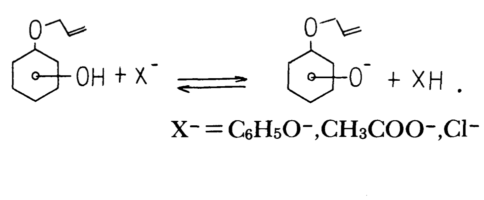
Fig. 3. The catalytic effect of alkali metal salts for the conversion of *o*-OH-APE at 145 °C (solv.: CH_3OH (potassium salt), $CH_3OH : H_2O = 1 : 1$ (sodium salt), salt: APE=0.5 : 1).

catalytic effect by sodium acetate is different from that by zinc chloride.

As shown in Fig. 3, the order of the catalytic effects by the alkali metal salts is

phenolate > acetate > chloride.

This order is the same as that of the basicities of the anion residues of the salts.[8] The degree of dissociation of the hydroxyl group of OH-APE is largest in the presence of phenolate and smallest in the presence of chloride:



$X^- = C_6H_5O^-, CH_3COO^-, Cl^-$

Table 1. Catalytic Effect of Alkali Metal Salts for the Conversion of *o*-OH-APE at 145 °C (Solv. CH_3OH)[a]

Reaction time/h	Catalytic effect/%		
	CH_3COOLi	CH_3COONa	CH_3COOK
0.5	26.9	10.0	3.0
1.0	43.3	20.2	8.3
1.5	48.8	24.6	12.5

a) CH_3COOM : APE=0.5 : 1.

Table 2. Conversion of *o*-OH-APE in the Presence of Alkali Metal Salts at 145 °C (Solv. CH_3OH)[a,b]

Salt	*o*/%	*p*/%	*p*/*o*	log (*p*/*o*)
None	16.5	9.5	0.58	−0.24
CH_3COOLi	20.8	48.5	2.33	0.37
CH_3COONa	19.4	26.8	1.38	0.14
CH_3COOK	17.3	17.0	0.98	−0.01
C_6H_5OK	18.0	52.4	2.91	0.46

a) Salt : *o*-OH-APE=0.5 : 1. b) Reaction time: 1 h.

For the change in metal ions (Table 1), the order is

Li salt > Na salt > K salt.

In methanol, the degree of solvation of metal ions increases with decreasing ionic radius.[9] This order seems parallel with the stability of the alkali metal ions in methanol. It is in agreement with the order of the degrees of dissociation of the alkali metal salts.

As shown in Table 2, the (para rearranged product)/(ortho rearranged product) value (*p*/*o* ratio) for *o*-OH-APE is increased by the addition of the alkali metal salts. The order of the magnitudes of the *p*/*o* ratios is

phenolate > acetate

and

Li salt > Na salt > K salt.

These orders agree with that of the catalytic effects. As stated in preceding paper,[1] the *p*/*o* ratio is closely

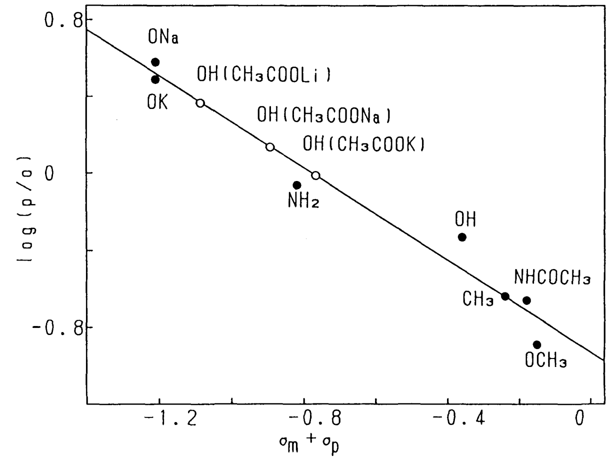
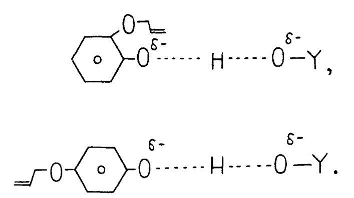


Fig. 4. The relationship between *p*-product to *o*-product (*p*/*o*) in *o*-X-APE and ($\sigma_m + \sigma_p$) (σ_m and σ_p values of -ONa and -OK are used in that of $-O^-$).

related to the value of substituent constant $(\sigma_m+\sigma_p)$.[10,11] A strongly electron-releasing substituent possesses a negative large value of $(\sigma_m+\sigma_p)$. For the rearrangement of an APE possessing such an electron-releasing substituent, the value of p/o ratio is large. As shown in Fig. 4, the value of $(\sigma_m+\sigma_p)$ of hydroxyl group alone is -0.36, and $\log(p/o)$ in the absence of alkali metal salt is -0.33. However, in the presence of the salt, $\log(p/o)$ is -0.01—0.37. This value corresponds to -0.77— -1.09 of $(\sigma_m+\sigma_p)$ (Fig. 4). The electron-releasing ability of hydroxyl group is increased by the addition of alkali metal salt. It seems that the value of $(\sigma_m+\sigma_p)$ of hydroxyl group increased by the addition of alkali metal salt is close to the values of $(\sigma_m+\sigma_p)$ of pheoxide ion (-O^-).

Consequently, the mechanism of the catalytic effect by the alkali metal salts may be interpreted as follows. The hydroxyl group of *o*(or *p*)-OH-APE is converted to phenoxide ion -O^- by the anion residue of the salt:



Y = COCH$_3$, C$_6$H$_5$

Therefore, in analogy with APEs bearing metal oxide groups,[1] the benzene ring is stabilized by the strong electron-releasing effect of phenoxide ion -O^-. (In the transition state, a positive charge is produced on the benzene ring of APE.[7]) In addition to the above effect, for *o*-isomer, another effect is to be considered: an intramolecular repulsion between the phenoxide ion -O^- and the ethereal oxygen of allyloxyl group. By this repulsion, the ground state is unstabilized and the activation energy for the rearrangement decreased.

For *o*-OH-APE, the rearrangement is accelerated by these two effects (the strong electron-releasing effect and the intramolecular repulsion effect). On the other hand, for *p*-isomer, only the strong electron-releasing effect is put into operation. Therefore, it is expected that the catalytic effect for *o*-OH-APE is larger than that for *p*-OH-APE. In fact, the experimental results agree with this assumption (Fig. 5). However, the difference in catalytic effect between *o*- and *p*-OH-APEs is not so large. The reactivity of *o*-OH-APE alone is much higher than that of *p*-OH-APE (Fig. 5) because, in *o*-OH-APE, an intramolecular hydrogen bond is formed between the hydroxyl group and the ethereal oxygen.[6] The negative charge of the ethereal oxygen produced in the transition state is reduced by this hydrogen bond.[6] But by the addition of alkali metal salt, the above intramolecular hydrogen bonding effect for *o*-OH-APE is caused to disappear. It seems that the observed catalytic effect for *o*-OH-APE by alkali metal salt is not so large as to be balanced by the profit and loss.

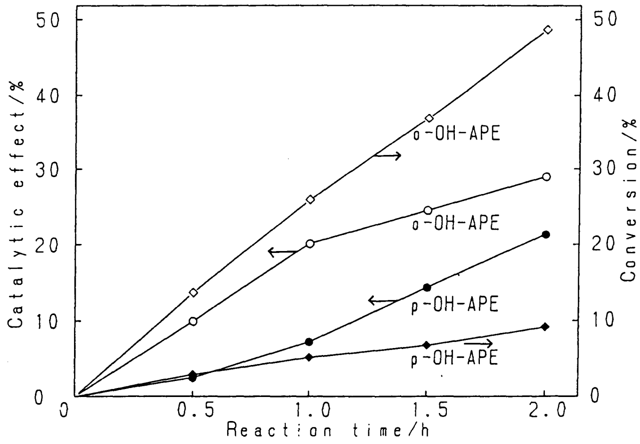


Fig. 5. The conversion and the catalytic effect of CH$_3$COONa for the conversion of *o*- and *p*-OH-APE at 145 °C (solv.: CH$_3$OH, salt: APE=0.5 : 1).

References

1) Part V: M. Goto, T. Hayashi, K. Goda, and Y. Okada, *Nippon Kagaku Kaishi,* **1986**, 1096.

2) W. N. White and E. F. Wolfarth, *J. Org. Chem.*, **35**, 2196 (1970).

3) H. L. Goering and R. R. Jacobson, *J. Am. Chem. Soc.*, **80**, 3277 (1958).

4) T. Hayashi and M. Goto, *Nippon Kagaku Kaishi,* **1978**, 1007.

5) T. Hayashi and M. Goto, *Nippon Kagaku Kaishi,* **1977**, 1512.

6) M. Goto and T. Hayashi, *Nippon Kagaku Kaishi,* **1986**, 49.

7) M. Goto and T. Hayashi, *Nippon Kagaku Kaishi,* **1979**, 743.

8) "Kagaku Binran," ed by the Chemical Society of Japan, Maruzen, Tokyo (1984), p. 343.

9) Z. Tokura, "Yobaiwa," Kagaku Dozin, Kyoto (1973), p. 28.

10) W. N. White, D. Gwynn, R. Schlitt, C. Girard, and W. Fife, *J. Am. Chem. Soc.*, **80**, 3271 (1958).

11) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).